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Carbamate stability measurements in amine/CO_2/water systems with Nuclear Magnetic Resonance (NMR) spectroscopy

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Abstract

NMR experiments were carried out for 30 mass % aqueous solutions of monoethanolmine (MEA), ethylenediamine (EDA) and piperazine (PZ) at 25 ºC. To distinguish between the amine/protonated amine and bicarbonate/carbonate pairs, an earlier method developed for primary amine (2-amino-2-methyl-1-propanol) was implemented. The amine protonation constant, the dissociation constant of carbonic acid from literature, and pH measurements for different ionic strengths, were all employed and the data were correlated with ionic strength.

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Keywords: diamine, NMR, carbamate, CO_2 capture

1. Introduction

CO_2 capture is based on the removal of carbon dioxide from power plants and large stationary industrial sources as these represent the best targets for emissions reduction. Various carbon capture and storage (CCS) technologies are available worldwide. Chemical absorption using amine base solvents is at present the most viable technology for CO_2 capture and has the potential to remain the most important process also in the future.
Amines are usually employed as absorbents for CO_2 capture and monoethanolamine (MEA), diisopropanolamine (DIPA), N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) are commonly used. However, due to problems associated with alkanolamines, such as their degradation in oxygen rich atmospheres,

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considerable energy need for solvent regeneration, environmental issues and recycling efficiency, the quest to find alternative candidates is very important [1, 2].

Carbamate stability is a very important parameter for determining the absorption capacity and regeneration energy requirement. The carbamate formation constant can be expressed as a product of carbamate formation ($AmCO_2^-$) in the system divided by the free amine (Am) and carbonate (HCO_3^-) species at a certain loading. The reported experimental data is very limited and scarce. Nuclear Magnetic Resonance (NMR) can certainly measure the species produced in the amine/CO_2/water system. However all species cannot be observed directly due to fast exchanging protons in the system [3-5]. To distinguish amine (Am) from protonated amine (AmH^+) and carbonate (CO_3^{2-}) from bicarbonate (HCO_3^-), different techniques were suggested, i.e. pH shift calibration and chemical shift calibration in NMR for the specific species [6-8]. Holmes, et al., (1998) [9] suggested an empirical correlation based on chemical shift of the carbonate and bicarbonate peaks in the NH_3/CO_2/water system. Jakobsen, et al., (2008) [10] suggested an empirical calibration correlation based on a changing of the chemical shift in amine/protonated amine and carbonate/bicarbonate by adding an acid. Very recently, Ciftja, et al., (2014) [11] proposed a method to separate amine/protonated amine and carbonate/bicarbonate by using a mass balance and electroneutrality. This method provides full liquid speciation by separating the carbonate/bicarbonate and amine/protonated amine based on pH measurements, ionic strength (I) and the pK_a of the different systems.

^{13}C-NMR was employed to study the carbamate formation and to estimate an apparent carbamate stability constant in aqueous solutions of CO_2 and monoethanolamine (MEA), ethylenediamine (EDA) and piperazine (PZ) at 25ºC. The direct liquid-phase speciation method is published in literature [4, 12] The activity coefficient model together with mass balance/electro neutrality are introduced to estimate the individual species, hence the carbamate formation constant can be derived.

The main objective of the paper is to verify the method implemented by Ciftja, et al., [11] with a known system such as monoethanolamine/CO_2/water as well as for diamine systems such as piperazine/CO_2/water and ethylenediamine/CO_2/water.

2. Methods and Materials

2.1. Chemicals

The chemicals with purity ≥ 99% used in this study, monoethanolamine (MEA), ethylenediamine (EDA), piperazine (PZ) and deuterium oxide (D_2O), all supplied from Aldrich and 1,4-dioxane (D8) from Fulka were used without any further purification. The amine solutions were prepared from distilled water by weight. The resulting solutions were loaded with CO_2 (grade 5.0) by bubbling of gas. The initial loading was estimated from the weight change of the solution after CO_2 bubbling and the final loading of the prepared solutions were analyzed for CO_2 and amine content. Their concentrations were determined by a titration/precipitation method and compared with the NMR results. The pH of each sample was measured using a Metrohm 827 pH Lab Meter. The pH - electrode was calibrated using pH buffers of 12 (± 0.02), 9 (± 0.02), and 4 (± 0.02), supplied by Mettler Toledo.

2.2. Sample preparation

Loaded and unloaded solutions of 30 mass % amine in water with volume about 0.4 mL were filled into 5 mm Norrel 507-HP tubes and weighed in a Mettler AE163 digital analytical balance with accuracy of ±0.0001g. A small amount of D_2O (5-10 mass % of solution) was added to obtain a signal lock. A GVLab fixed-speed vortex mixer was used to mix all the contents in the NMR tubes.

A standard of 1,4-dioxane (5% of the total mass of solution) was added to provide a sharp peak with a known chemical shift in the NMR spectrum and positioned in a region distant from the sample peaks. All the spectra analyzed were calibrated based on the chemical shift of 3.75 ppm for proton NMR and of 67.19 ppm for carbon NMR [13]. All the NMR spectra were recorded on a Bruker Avance 400 DPX spectrometer at 25 ºC.

2.3. NMR experiments

The NMR experiment started with assignments of the signals present in each of the amine/CO_2/water systems which involve 1D and 2D NMR experiments [4, 14]. Quantitative ^{13}C NMR experiments were implemented to find the concentration of the species in each of the systems. Here, inverse gated decoupling and pulse repetition time was adjusted to at least 5 times T_1 of the slowest relaxing nuclei in the sample. T_1 times were determined by the inversion recovery method. Therefore, the specific conditions regarding relaxation time in the experiments were fulfilled Ciftja et al., [4].

3. Chemistry of the system

When CO_2 is absorbed into an aqueous amine solution, the base reactions taking place in the system can be represented by these reactions:

Dissociation of water:

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad (1)$$

Dissociation of dissolved CO_2 through carbonic acid:

$$2H_2O + CO_2 \leftrightarrow H_3O + HCO_3^- \quad (2)$$

Dissociation of bicarbonate:

$$HCO_3^- + H_2O \leftrightarrow H_3O + CO_3^{2-} \quad (3)$$

Dissociation of protonated amine (AmH^+)

$$AmH^+ + H_2O \leftrightarrow Am + H_3O^+ \quad (4)$$

Dissociation of diprotonated diamine (AmH_2^{2+}):

$$AmH_2^{2+} + H_2O \leftrightarrow AmH^+ + H_3O^+ \quad (5)$$

Carbamate hydrolysis:

$$Am + HCO_3^- \leftrightarrow AmCO_2^- + H_2O \quad (6)$$

Dicarbamate formation:

$$AmCO_2^- + CO_2 + H_2O \leftrightarrow Am(CO_2)_2^{2-} + H_3O^+ \quad (7)$$

The ions produced from the chemical reaction of carbon dioxide and aqueous solutions of amine are: Am, AmH^+, $AmH^+CO_2^-$, AmH_2^{2+}, $AmCO_2^{2-}$, $Am(CO_2)_2^{2-}$, CO_3^{2-}, HCO_3^-, H_2O, H_3O^+ and OH^-.

4. Results and discussions

4.1. The method of splitting NMR species

The peak assignments and the direct liquid phase species concentrations obtained from NMR spectroscopy for 30 mass % aqueous solution of MEA, EDA or PZ/CO_2/H_2O systems, are given in the literature [4, 12]. To distinguish a free amine/protonated amine and carbonate/bicarbonate species, a method was developed as described by Ciftja et

al., [11]. The method was only used for loaded solutions of a mono amine, 2-amino-2-methyl-1-propanol (AMP) at three different temperatures [11]. In the present work we implement the method described by Ciftja et al., [11] but use diamine systems such as ethylenediamine and piperazine at different CO_2 loadings and different ionic strengths. This approach can be improved by calculating the activity coefficients of each species as briefly described below:

a) Liquid-phase speciation obtained directly from NMR: (n_{Am/AmH^+}), ($n_{AmCO_2^{2-}}$), ($n_{Am(CO_2^-)_2}$) and ($n_{HCO_3^-/CO_2^{2-}}$) at a certain loading and measured pH of solution (a_{H^+}).

b) Material balance for amine:

$$n^{o}_{Am} = n_{Am} + n_{AmH^+} + n_{AmCO_2^-} + n_{Am(CO_2^-)_2} \quad (8)$$

c) Material balance for CO_2:

$$n^{\circ}_{CO_2} = n_{AmCO_2^-} + n_{HCO_3^-} + n_{CO_3^{2-}} + 2 \cdot n_{Am(CO_2^-)_2} \quad (9)$$

d) Electro-neutrality :

$$n_{AmH^+} + n_{H^+} = n_{AmCO_2^-} + 2 \cdot n_{Am(CO_2^-)_2} + n_{HCO_3^-} + 2 \cdot n_{CO_3^{2-}} \quad (10)$$

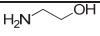
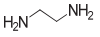
e) A simple activity coefficient model can be implemented to account for the ionic strength:

$$\ln \gamma_i = -\frac{A_D \cdot z_i^2 \cdot \sqrt{I}}{1 + B_D \cdot k_i \cdot \sqrt{I}} \quad (11)$$

n_i^0 represents the total mol of species whereas n_i, indicates the actual mole number of species per kg solution. The values from NMR are of the summed unprotonated and protonated species due to the inability of NMR to show them as separate signals.

Protonation constants of amines and for bicarbonate/carbonate are given in literature (Table 1). Then all the species can be determined with mass balances of amine and CO_2, electro-neutrality together with the activity coefficient of each species.

Table 1. Protonation constant of the chemicals at 25°C.

Chemical name /Abbreviation	Structure	p*K*a$_1$	p*K*a$_2$	Reference
Monoethanolamine /MEA		-	9.50	[16]
Ethylenediamine /EDA		9.93	6.85	[17]
Piperazine /PZ		9.71	5.41	[16]
HCO_3^-		-	9.74	[18]

4.2. Full-liquid speciation

To determine the full-liquid phase separation, a mass balance for amine (Eq. 8), CO_2 (Eq. 9) and the electro-neutrality (Eq. 10) were used together with the method developed previously by Ciftja et al., (2014) [11] .
The direct NMR speciation for MEA, EDA and PZ-CO_2-H_2O systems, are given in literature [4, 12]. Figure 1 shows the full liquid speciation distribution in the amine-CO_2-H_2O systems based on the proposed method for separation of the HCO_3^-/CO_3^{2-} and AMP/AMPH$^+$ peaks [11].

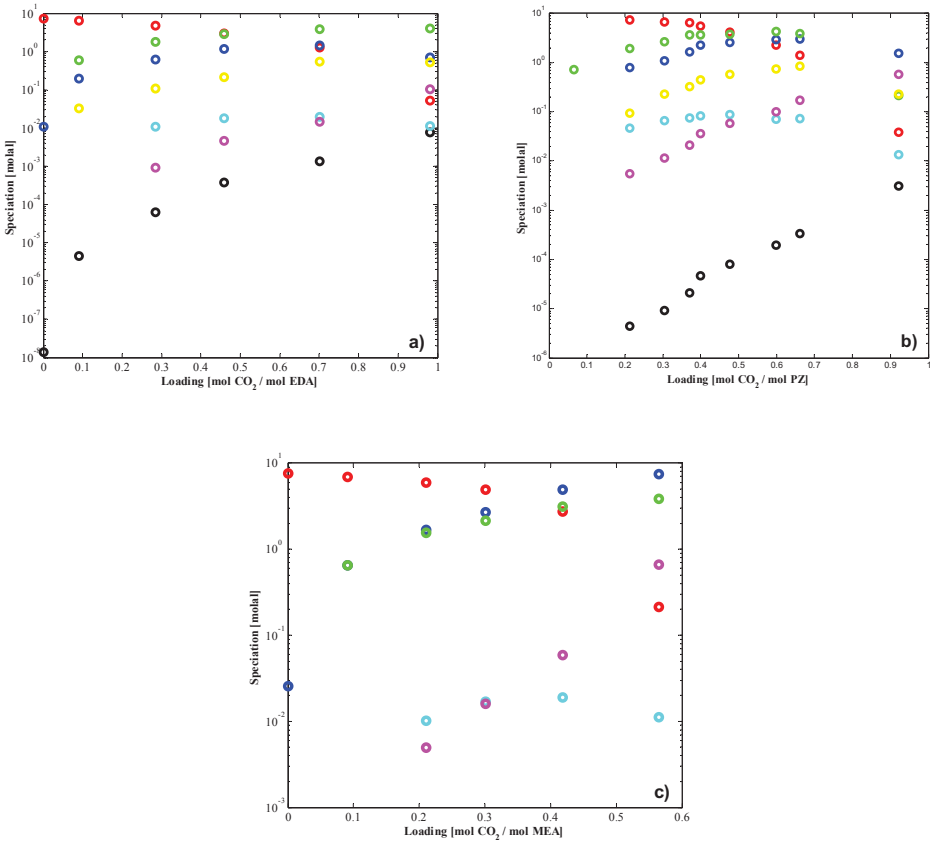


Fig. 1. Full liquid-phase speciation at 25 ºC. (a) EDA; (b) PZ; (c) MEA.
Symbols: O, Am ; O, AmH^+; O, AmH_2^{2+}; O, $AmCO_2^{2-}$; O, $Am(CO_2)_2^{2-}$; O, CO_3^{2-}; O, HCO_3^-.

Fig. 1 (a-c) shows that the reaction products in the amine-CO_2-H_2O systems are predominantly the carbamate species (O symbols) in the loading range up to about 0.4-0.6, and then starts decreasing at high CO_2 loading. This is plausible since the pH is still high. Above this value, the bicarbonate (O symbols) takes over. The level of carbamate formation (O, $AmCO_2^{2-}$) ranges in order: PZ > EDA > MEA whereas the bicarbonate formation (O, HCO_3^-) ranges in order: MEA > PZ > EDA.

4.3. Carbamate stability constant

Based on the carbamate hydrolysis reaction, Eq. 6, and the individual species concentrations obtained from the present work, an apparent concentration based carbamate stability constant can be calculated using Eq. 12.

$$K_C = \frac{[AmCO_2^-]}{[HCO_3^-][Am]} \qquad (12)$$

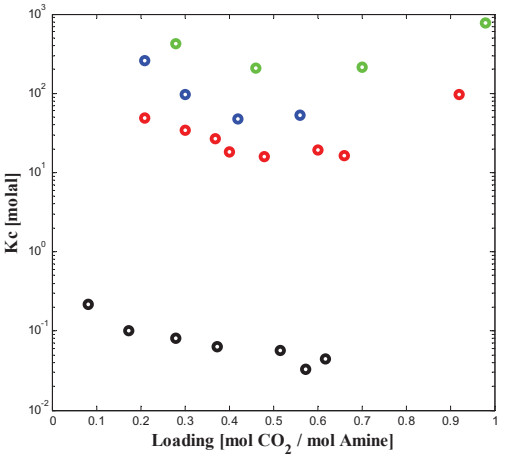


Fig. 2. Apparent carbamate stability constants (K_C) at 25 ºC. Symbols: ○, PZ ; ○,MEA; ○, EDA and ○, AMP from literature [11].

Figure 2 shows the carbamate stability constant at 25ºC, on molal basis, for the three different systems studied in the present work including carbamate stability data for AMP-CO_2-H_2O from literature [11].
By comparing all the systems, primary monoamines (AMP, MEA) and primary and secondary diamines (EDA, PZ) , we see that the apparent carbamate stability constant decreases with increasing CO_2 loading up to 0.5-0.6 and then increases as the loading increases. The apparent carbamate stability (K_C) in these systems increases in the order: AMP - PZ - MEA - EDA. This can be explained by the fact that the carbamate formation is higher in primary amines such as monoamine (MEA) and diamine (EDA) (see Fig. 1) and lower in a sterically hindered amine such as AMP. While the secondary diamine (PZ) has high affinity towards CO_2, the bicarbonate formation is higher than for MEA or EDA and this leads to a lower carbamate stability constant (K_C).

4. Conclusions

In the present work, carbamate formation for 30 mass % amine (MEA, EDA and PZ) at different CO_2 loadings and at 25 ºC was investigated experimentally by quantitative ^{13}C NMR.

Full liquid-phase speciations obtained based on pH measurements, ionic strength and pK_a of the amine-CO_2-H_2O systems, separating the carbonate/bicarbonate and amine/protonated amine were calculated and reported.

Apparent carbamate stability constants (K_C) are calculated for three different systems: MEA-CO_2-H_2O, EDA-CO_2-H_2O and PZ-CO_2-H_2O at 25ºC.

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